

Potential Energy Surface for H₂ Dissociation over Pd(100)

S. Wilke* and M. Scheffler

Fritz-Haber-Institut der MPG

Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany.

(submitted)

The potential energy surface (PES) of dissociative adsorption of H₂ on Pd(100) is investigated using density functional theory and the full-potential linear augmented plane wave (FP-LAPW) method. Several dissociation pathways are identified which have a vanishing energy barrier. A pronounced dependence of the potential energy on “cartwheel” rotations of the molecular axis is found. The calculated PES shows no indication of the presence of a precursor state in front of the surface. Both results indicate that steering effects determine the observed decrease of the sticking coefficient at low energies of the H₂ molecules. We show that the topology of the PES is related to the dependence of the covalent H(*s*)-Pd(*d*) interactions on the orientation of the H₂ molecule.

PACS: 68.10Jy, 68.35Dv, 73.20At, 82.65Jv

I. INTRODUCTION

Hydrogen dissociation on metal surfaces has become one of the benchmark systems for the understanding of dissociative adsorption processes. The H₂ / Pd system is particularly interesting as an example of non-activated dissociation over a transition metal surface. The dissociation process has been studied using molecular beam adsorption experiments¹ as well as state resolved time-of-flight measurements of desorbing hydrogen molecules²⁻⁵.

Hydrogen molecules dissociate spontaneously at Pd(100), i.e. molecules with low kinetic energy dissociatively adsorb at Pd(100) surfaces with a large initial sticking coefficient^{1,6}. The preference of non-activated dissociation pathways for low kinetic energies of the H₂ molecules is also consistent with the independence of the initial sticking coefficient on incident angle Θ as well as with the measured Maxwell-Boltzmann velocity distribution of desorbing H₂ molecules which corresponds to the surface temperature of the palladium substrate^{5,7}.

There are, however, clear indications that activated pathways exist as well. After a decrease for beam energies below ≈ 0.15 eV the initial sticking coefficient continuously increases¹. At those larger kinetic energies the dependence of the initial sticking coefficient on the incident angle of the molecules changes into a $\cos^{n-1}(\Theta)$ behavior with n increasing up to $n \approx 1.6$ for beam energies of 0.4 eV. State resolved desorption experiments show that the occupancy of the first vibrational excitation is significantly higher than that corresponding to a gas of hydrogen molecules in equilibrium with the surface temperature^{2,4,5}. This finding is called vibrational

heating. On the other hand, the rotational degrees of freedom are occupied less than what the surface temperature would imply (rotational cooling)³. In order to explain the vibrational heating, the values for $n > 1$ in the angular distribution, as well as the increase of the sticking coefficient with the kinetic energy of the H₂ molecules it has been found necessary in dynamic studies on two-dimensional model potential-energy surfaces (PES) to assume the presence of a small (about 0.1 eV) barrier in the *exit channel*, i.e. in the region of the reaction pathway where the H-H bond is already significantly stretched^{4,8}. Such an energy barrier, however, yields an additional kinetic energy of thermally desorbing molecules which has not been measured experimentally⁴.

There has been a long debate about the origin of the initial decrease of the initial sticking coefficient with increasing beam energies. Such a decrease and the observed dependence of the initial sticking coefficient on the angle of incidence with a coefficient $n \leq 1$ have been usually assigned to the presence of a weak, metastable molecular bound state of the H₂ molecule in large distance from the surface (precursor state)^{1,10,11,9}. The presence of a precursor state has also been assumed in order to explain the slow decrease of the sticking coefficient with hydrogen coverage⁶. An alternative explanation relates the initial decrease to the presence of both activated and non-activated dissociation pathways on the PES¹²⁻¹⁴. At low kinetic energies molecules with unfavorable orientations may reorientate during the dissociation process and follow a non-activated pathway but with increasing kinetic energy this steering is more and more hindered and the number of molecules proceeding along activated pathways increases.

The fundamental understanding of the dissociative adsorption of hydrogen rests on the knowledge of the PES which, as will be stressed below, depends rather crucially on all six coordinates of the two hydrogen atoms of the H₂ molecule. Experimental data have been interpreted in terms of simple, often two-dimensional model PES as discussed above. Very recently, accurate density functional calculation (DFT) of PES¹⁵⁻¹⁹ and high-dimensional quantum-dynamical simulations^{14,20-22} of H₂ dissociation have become available thus opening the way for complete *ab initio* investigations of dissociative adsorption and associative desorption processes. Previous DFT studies of the H₂ interaction with metal surfaces concentrated mainly on system where the dissociation is activated. There are a few studies of the interaction of H₂ molecules in front of surfaces of transition

metals with a partly filled d -states^{15,18,19}. In the recent work of White and Bird¹⁹ investigating hydrogen dissociation on W(100) the presence of non-activated dissociation pathways was confirmed but in dependence of the center-of-mass position of the molecule in the surface unit cell even for the most favorable orientation of the molecular axis activated dissociation has been obtained as well. Molecules with its axis perpendicular to the surface have been found to experience no attractive interaction. Summarizing their results, White and Bird expect molecular steering to play an important role in the dissociation dynamics at low incident energies.

In this paper we present and discuss detailed calculations of the potential energy surface for hydrogen dissociation on Pd(100). Here we analyze the physical properties behind the topology of the PES. We note that the results are now sufficiently complete for a six-dimensional quantum-dynamical simulation of the dissociation of H₂ molecules on Pd(100)²².

II. CALCULATION METHOD

The calculations have been performed using density-functional theory within the generalized gradient approximation (GGA)²³ and the full potential linear augmented plane wave method (FP-LAPW)^{24,25}. The application of the GGA is of crucial importance for the calculation of PES of hydrogen dissociation^{16,26,27}, but some important questions concerning the accuracy of PES calculated applying the GGA remain²⁸. The good agreement of experimental data with the results of high-dimensional quantum-dynamical simulation of H₂ dissociation based on the calculated PES for H₂/Cu(111)²⁰ and the PES presented in this paper²² shows that the GGA reproduces the important features of these PES with sufficient accuracy.

The FP-LAPW wave functions in the interstitial region are represented using a plane wave expansion up to $E_{\text{cut}}=11$ Ry, and due to the small radius of the muffin-tin sphere around H atoms ($r_{\text{MT}}^{\text{H}}=0.37$ Å) it is necessary to take into account plane waves up to $\tilde{E}_{\text{cut}}=169$ Ry for the potential representation²⁵. Inside the muffin-tin spheres the wave functions are expanded in spherical harmonics with $l_{\text{max}}=10$, and non-spherical components of the density and potential are included up to $l_{\text{max}}=3$. For the \mathbf{k} -integration we used 64 uniformly spaced points in the two-dimensional Brillouin zone corresponding to the $c(2\times 2)$ surface unit cell. All calculations were performed non-relativistically.

In the calculations we used a supercell geometry. The metal substrate is modeled by three layers slabs which are separated by a 10 Å thick vacuum region. Hydrogen molecules are placed at both sides of the slab. We used a rigid substrate because due to the large mass ratio between Pd and H the substrate will not change during the scattering event. The slab thickness of only three layers

has been chosen with respect to the large computational demand of the evaluation of the PES. The application of such small layer thickness for the Pd(100) substrate gives an acceptable accuracy of the PES because due to the large density of states at the Fermi energy perturbations in the electronic structure induced by the impinging H₂ molecule are screened very effectively. We confirmed this by increasing the layer thickness of the substrate to 5 layers and comparing the total energy with respect to the separated H₂ and Pd(100) surface at various points of the reaction pathways. We found that in the region of the PES where the H₂ molecule approaches the surface and starts to dissociate the differences of the potential energy are less than 0.05 eV per H₂ molecule. In particular, the character of the dissociation pathway, whether it is activated or non-activated, is not influenced. This part of the PES determines the dynamics dissociation of the hydrogen molecule²². The dependence of the adsorption energy on the layer thickness is more pronounced in the region of the PES corresponding to adsorbed H atoms and strong H-Pd bonds. Here, the energy changes with increasing layer thickness up to 0.12 eV per H₂ molecule.

The application of such a small layer thickness for the Pd(100) substrate is possible because due to the large density of states at the Fermi energy perturbations in the surface electronic structure induced by the impinging H₂ molecule are screened very effectively. We confirmed this by increasing the layer thickness of the substrate to 5 layers and comparing the total energy with respect to the separated and Pd(100) surface to that of the three layer calculations at various points of the reaction pathways. We found that the differences in the potential energies are below 0.12 eV and that the changes are considerably smaller for larger heights of the molecule above the surface. For the PES calculation we employed a supercell with a $c(2\times 2)$ surface structure. However, in the case of the geometry where the H₂ hits an on-top site and dissociates into two hollow positions H atoms belonging to H₂ molecules in different surface unit cells within a $c(2\times 2)$ structure would come too close during the dissociation process and the unit cell has been enlarged to a $p(2\times 2)$ structure. The convergence of our results was tested using a $p(2\times 2)$ surface unit cell, a plane-wave cut-off for the wavefunctions expansion of $E_{\text{cut}}=13$ Ry and a larger H muffin tin radius $r_{\text{MT}}^{\text{H}}=0.48$ Å in the exit channel region. The resulting changes of the potential energy were again found to be less than 0.08 eV per H₂ molecule.

The potential energy of a hydrogen molecule as it is used throughout the paper is defined as the DFT-GGA total energy. The energy zero is the energy of the geometry difference where the molecule is sufficiently far away from the surface, ($Z=3.7$ Å), such that there is practically no interaction between the molecule and the surface. Zero point corrections and other vibrations are not included in the PES.

III. RESULTS

First, we briefly summarize the properties of bulk Pd, the clean Pd(100) surface, and adsorbed hydrogen atoms^{29,30}. The calculated lattice constant of Pd calculated by the DFT-GGA is 4.03 Å. This value is 3 % larger than the lattice constant obtained within the LDA, and 3.5 % larger than the experimental value²⁹. The clean Pd(100) surface shows a slight inward relaxation of the topmost Pd layer of -0.9 % of the bulk interlayer distance. This value is close to the relaxation of -0.6 % obtained by DFT-LDA calculation²⁹. The equilibrium position of the hydrogen is the surface hollow site with a small adsorption height $Z_0=0.1$ Å²⁹. At the bridge site the adsorption energy is about 0.3 eV less favorable and the adsorption height increases to $Z_0=1.3$ Å. Adsorption at the on-top position is even unstable against associative desorption²⁹. Obviously, this pronounced dependence of the H – Pd bond strength on the geometry of the H adatom effects the potential energy during the dissociation process as will be discussed below.

Assuming that the positions of the substrate metal atoms can be kept fixed the PES of hydrogen dissociation depends on the six coordinates defining the position of the two hydrogen atoms of the H₂ molecule. Figure 1

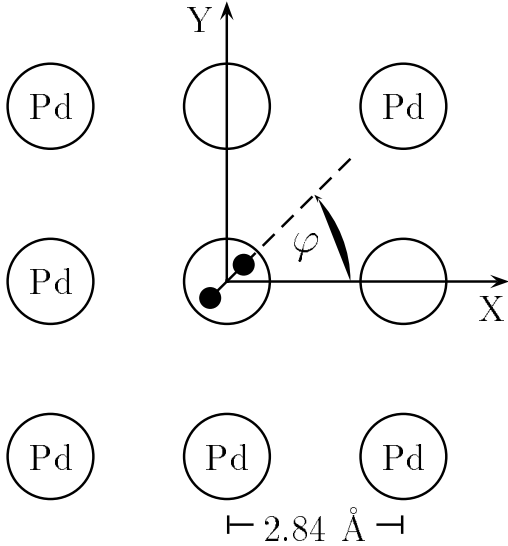


FIG. 1. Coordinate system used to describe the orientation of the H₂ molecule with respect to the surface Pd atoms. The height of the H–H center of mass above the surface is Z , the H–H distance is $d_{\text{H-H}}$, and the angle of the molecular axis with the surface normal is θ .

shows the coordinate system used to describe the position and orientation of the H₂ molecule. The center of mass position is given by the three cartesian coordinates (X, Y, Z) for which the origin is at the center of a surface Pd atom. The two rotational degrees of freedom are given by the angle of the molecular axis with the Z -axis θ (cartwheel rotation) and with the X -direction φ (he-

licopter rotation). The distance between the hydrogen atoms is denoted by $d_{\text{H-H}}$.

In order to investigate possible non-activated pathways Fig. 2 gives

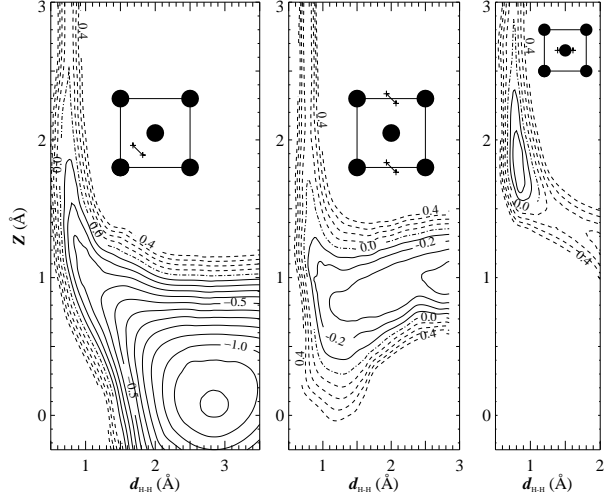


FIG. 2. Cut through the six-dimensional potential energy surface (PES) of a H₂ molecule in front of Pd(100). We display “elbow plots” where Z is the height of the H₂ center of mass over the surface, and $d_{\text{H-H}}$ is the distance between the two hydrogen atoms. The cut is defined by keeping the molecule parallel to the surface at an azimuthal orientation shown in the inset. The units of the potential energy are eV and the interval between adjacent contour lines is 0.1 eV.

the PES as functions of H–H distance, $d_{\text{H-H}}$, and the molecular center-of-mass distance from the surface, Z , for fixed, characteristic positions of the molecules center-of-mass in the surface unit cell: the bridge ($X=0, Y=0.5$ $d_{\text{Pd-Pd}}$, $\varphi=0^\circ$)(a), the hollow (b) ($X=Y=0.5$ $d_{\text{Pd-Pd}}$, $\varphi=0^\circ$) and the on-top ($X=Y=0$, $\varphi=45^\circ$)(c) site. The molecular axis is kept parallel to the surface ($\theta=90^\circ$). For all geometries investigated in Fig. 2 this $\theta=90^\circ$ orientation is the energetically most favorable one (see also Fig. 3 below). The dissociation over the

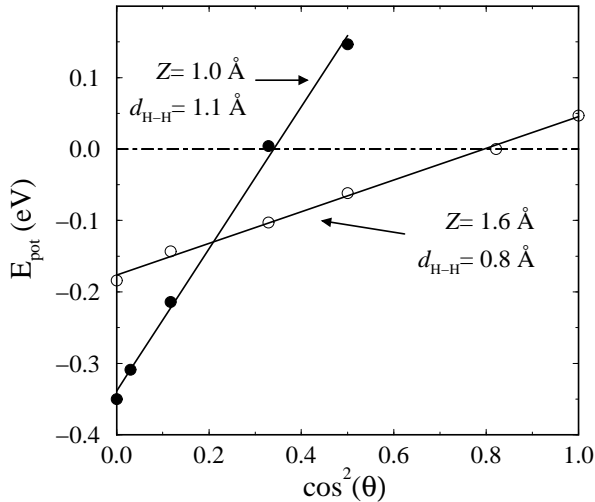


FIG. 3. Dependence of the potential energy of an H_2 molecule on the angle θ of its molecular axis with the surface normal. The geometry for $\theta=90^\circ$ corresponds to Fig. 2a. The molecule is in the entrance channel at ($Z=1.6 \text{ Å}$, $d_{\text{H-H}}=0.8 \text{ Å}$) (open circles) or in the exit channel at ($Z=1.0 \text{ Å}$, $d_{\text{H-H}}=1.1 \text{ Å}$) (filled circles)

bridge (Fig. 2a) and over the hollow site (Fig. 2b) is non-activated and proceeds with a continuous gain of energy without a hampering energy barrier. The dissociation of an hydrogen molecule over the on-top site with fixed coordinates ($X=0$, $Y=0$) is activated. The barrier has an energy of about 0.15 eV and is situated in the exit channel region. Figure 2 shows that non-activated dissociation of H_2 molecules on Pd(100) is possible over several non-activated pathways including a large region of center-of-mass positions of the hydrogen molecule in the surface unit cell.

The two-dimensional cuts through the PES in Fig. 2 refer to the situation that the orientation of the molecular axis is *fixed*. In reality the impinging hydrogen molecule rotates. In the following we discuss the dependence of the potential energy on the orientation of the molecular axis, i.e. on the angles θ and φ .

The change of the orientations the molecular axis with respect to the surface normal, θ , and away from $\theta=90^\circ$, implies a significant increase of the potential energy. Figure 3 displays the change of the potential energy of a H_2 molecule in dependence of the angle θ of the molecular axis with the surface normal for two positions in the PES of Fig. 2a; all other parameters being fixed. For both distances, $Z=1.6 \text{ Å}$ and $Z=1 \text{ Å}$ the potential energy increases like $\cos^2(\theta)$. Fig. 3 shows that with decreasing distance to the surface a minimum in the dependence of the potential energy with angle θ with increasing depth develops. The “cartwheel” rotations are more and more hindered. There is, however, a large difference between the “entrance” channel region, where the hydrogen molecule approaches the surface and the H_2 bond is still intact and the “exit” channel region where the H–H bonds is stretched and the dissociation of the molecule

starts. In the entrance channel, at larger heights Z (see open circles in Fig. 3), there is no or only a small repulsive interaction of the molecule with the surface even for a configuration with the molecular axis perpendicular to the surface $\theta=0^\circ$. Thus, the hydrogen molecules may approach the Pd(100) surface without an appreciable loss in energy and independent of their initial rotational state. In the exit channel where bonds of the hydrogen atoms with the surface form the potential energy depends sensitively on the orientation θ (see filled circles in Fig. 3) and the interaction of the molecule with the surface becomes repulsive already for small deviations from $\theta=90^\circ$. These conclusion are confirmed for the extreme case of a hydrogen molecule hitting the surface at the hollow site with its axis fixed perpendicular to the surface. We find that in the entrance channel the downmost hydrogen atom may approach the surface plane without a substantially barrier but for *fixed* orientation of the molecular axis at $\theta=0^\circ$ the potential energy increases drastically if the H–H bond is stretched and a nearly classical hard wall potential blocks the exit channel. Without any steering of the molecular axis during the dissociation non-activated dissociation pathways are possible only for molecules entering the exit channel region within a narrow region of orientations θ of the molecular axis and low initial sticking coefficient would result.

We expect, however, that the steering of the molecular axis toward energetically favorable orientations is rather effective. At low kinetic energies the rotational period of the molecule is comparable to the time the molecule spends at distances Z corresponding to the end of the entrance channel. A molecule with a kinetic energy of $E_{\text{kin}}=0.05 \text{ eV}$ travels 0.6 Å per 0.03 ps and when it is in the $j=2$ rotational state it rotates during this time (or pathway) by about 90° . The large increase of the potential energy with angle θ in Fig. 3 at the end of the entrance channel corresponds to large forces aligning the molecular axis towards orientations where the dissociation becomes energetically favorable (“steering effect”). With increasing beam energy in the adsorption experiments¹ both the kinetic and rotational energy of the molecules increases. This shortens the time the molecule spends at the end of the entrance channel and it becomes more likely that the molecule is reflected before the axis is aligned. An increase of the rotational energy implies that states with shorter rotational periods are occupied and those molecules turn out of the favorable orientation again more easily. As a consequence of the reduced steering the initial sticking coefficient reduces^{1,22}.

In the high symmetry configurations shown in Fig. 2 the most favorable orientation of the H_2 molecule is that where the molecular axis is parallel to the surface ($\theta=90^\circ$). For other center-of-mass positions and orientations φ of the molecule the minimum of the potential energy with respect to the angle θ deviates from $\theta=90^\circ$. As an example, if the center of mass of the molecule is between the hollow and bridge position ($X=0.25 d_{\text{Pd-Pd}}$, $Y=0.5 d_{\text{Pd-Pd}}$, $\varphi=0^\circ$) the optimal angle at a height

$Z=1.1$ Å is $\theta=65^\circ$, i.e. the H atom pointing toward to hollow site is closer to the surface than that pointing toward the bridge site. This tilting of the molecular axis is consistent with the different adsorption height of hydrogen adatoms at the hollow and bridge adsorption site. The potential energy is -0.3 eV, a value between that found along the reaction pathway for a center of mass-position over the bridge (Fig. 2a) and hollow site (Fig. 2b) at this height. Generally, the energetically most favorable orientation of the molecular axis, θ , optimizes the H-surface bond strength of both H atoms of the H_2 molecule.

In the case of “helicopter” rotations a pronounced decrease of the potential energy is found for geometries where H and Pd atoms get closer than a typical H-Pd bond length (1.7 Å). These geometrical constraints affect different positions in the surface unit cell differently. Dissociation over the bridge site is non-activated in the geometry shown in Fig. 2a ($\varphi=0^\circ$). In the case that the hydrogen atoms are oriented towards the Pd atoms ($\varphi=90^\circ$) helicopter rotations are not hindered only at large distances Z . For this configuration a steep increase of the potential energy is found already at the end of the entrance channel ($Z=1.2$ Å, $d_{H-H}=0.9$ Å). The H-Pd distance is 1.54 Å and the potential energy for H atoms orientated towards the Pd atoms is $E_{\text{pot}}=+0.25$ eV, i.e. 0.57 eV higher than in geometry with the H atoms oriented toward the hollow sites (see Fig 2a). In the case that the center of mass position of the impinging molecule is over the hollow site helicopter rotations are not hindered. A substantial increase of the potential energy for the orientation of the molecule with the H atoms oriented toward the surface Pd atoms ($\varphi=45^\circ$) is found only in the exit channel where the H-H bond is already broken and both H atoms may easily reorientate separately. In difference to the “cartwheel” rotations the importance of the steering of the impinging hydrogen molecule into favorable orientations φ of the molecular axis will depend on the position of the molecule in the surface unit cell.

Metastable, weakly bound molecular states of H_2 which may act as precursor states to the dissociation of the molecule are commonly assumed to arise due to an interplay the repulsive Pauli repulsion between the closed shell electronic configuration of H_2 and the tails of the metal surface electronic states and the attractive van der Waals interaction⁹. In our calculations there is no indication of local minimum of the potential energy related to such types of precursor states at large distances in front of the Pd(100) surface. Although the long-range tail of the van der Waals interaction related to polarization fluctuations are not described within the GGA recent calculations of the PES of He atoms in front of Rh(100) have shown³¹, that the GGA is capable to adequately reproduce weakly bound states of adsorbates with a closed shell electronic configuration. The absence of a considerable repulsive interaction of the impinging H_2 molecule with the surface at larger distances Z even for unfavorable orientations of the molecular axis and the

large decrease of the potential energy already at distances $Z \approx 2$ Å found in Fig. 2 make this mechanism of the formation of molecular bound states in front of the metal surface rather improbable.

Local minima in a restricted subspace of the high-dimensional PES, may arise not only at large distances in front of the surface due to the interplay of the Pauli repulsion and attractive van-der Waals interaction but also at distances Z where the direct H-metal interaction dominates. They are a consequence of the pronounced dependence of the H-metal bond on the orientation of the molecule and the H-surface-metal-atom distances. For an example, the dissociation pathway on top of a Pd surface atom (Fig. 2c) shows a minimum of E_{pot} in the entrance channel for *fixed* center-of-mass position of the molecule.

A more detailed investigation of the dissociation over the on-top site shows that the minimum of potential energy seen in Fig. 1c is *not* a local minimum in the PES. The molecule can follow a purely attractive pathway if its center-of-mass position is able to relax in order to optimize the H-Pd bonding. Figure 4 shows the variation of the potential energy for

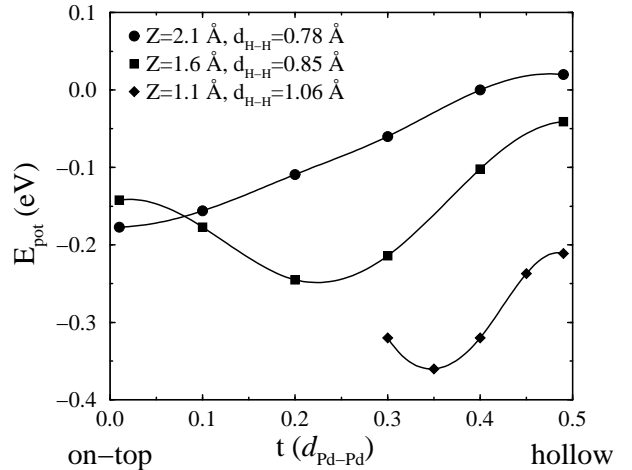


FIG. 4. Dependence of the potential energy of H_2 on its center-of-mass-position along a path $R=(X=-t, Y=t, Z=\text{constant})$ for three heights of the molecule. The molecular axis is parallel to the surface ($\theta=90^\circ$) and the angle φ is fixed at $\varphi=45^\circ$. The point $t=0$ corresponds to the geometry in Fig. 2c.

different heights Z in the case that the center-of-mass coordinate is changed along a path, t , $R=(X=-t, Y=t, Z=\text{constant})$. At large distances $Z > 1.8$ Å a position on-top of the surface Pd atom ($t=0$) is most favorable. At smaller heights the optimal reaction pathway involves a motion of the center-of-mass position towards the hollow sites. This geometry for lower Z is similar to the energetically most favorable orientation of a H_2 molecule in front of a Rh(100) surface¹⁵.

It is interesting to compare the PES of hydrogen dissociation on W(100)¹⁹ with that on Pd(100). Both sub-

strates are transition metals but tungsten and palladium crystalize into different lattice types (W is bcc, and Pd is fcc). Furthermore, W is in the middle of the $5d$ and Pd at the end of the $4d$ transition metal series. The PES of hydrogen dissociation on Pd(100) and on W(100)¹⁹, however, is qualitatively similar. Both PES exhibit several non-activated dissociation pathways. The pronounced dependence of the potential energy on the orientation of the molecule with respect to the surface metal atoms, especially on “cartwheel” rotations, is found also on W(100). There are also characteristic differences between both PES. This is already documented in the different equilibrium adsorption site, which is at the bridge position on W(100) in contrast to the hollow site on Pd(100). The geometry of the non-activated dissociation pathways on both surfaces is different. For example the dissociation with fixed center of mass position over the hollow site has an energy barrier of 0.3 eV on W(100) but no barrier on Pd(100). These differences will influence details of the dynamics of the hydrogen molecules on the PES. The calculations confirm, however, that the central features of the PES of hydrogen dissociation, e.g. the presence of non-activated dissociation pathways, are determined by the presence of a partly filled d -band in the electronic structure of both transition metal substrates.

IV. BREAKING OF THE MOLECULAR BOND AND MAKING OF NEW ADATOM-SURFACE BONDS

The large reactivity of transition metals for hydrogen dissociation given by the presence of dissociation pathways with no or only small energy barriers is actuated by a partly filled d -band^{15,18,32–36}. The mechanism how the d -band may affect the energetics of hydrogen dissociation has been interpreted in different ways. Within the Harris-Andersson model³² the repulsive interaction and the formation of barriers for H_2 dissociation on surfaces of simple and noble metals is, based on the work of Zaremba and Kohn³⁷, related the Pauli repulsion between the closed shell configuration of the H_2 molecule and the tails of the s, p -waves of the surface electronic structure. At transition metal surfaces the Pauli repulsion is suppressed by a low-energy occupation redistribution of electrons out of the s, p -tails into the large density of holes in the d -band just above the Fermi energy. Thus there is no direct interaction with the metal d -states and the dissociation barriers are governed by the interaction at large distances to the surface. The analysis of PES of hydrogen dissociation on various metal surfaces has shown that the top of the energy barriers occurs in the *exit channel*, i.e. at a point where the H–H interaction is significantly weakened and strong H–metal bonds are already being formed^{18,34}. Those results, which are not consistent with the Harris-Andersson model³², have been consistently explained within a reactivity model^{18,34,38}

related to the frontier orbital concept^{33,39}. Superimposed to the interaction of the hydrogen molecule with the s, p -states of the metal, which gives rise to energy barriers found at simple metals, there is a contribution due to the direct interaction of H_2 with the metal d -states. It is repulsive as long as both the bonding and the antibonding states of the interaction of the H_2 σ_g -orbital with the metal d -bands are occupied but becomes attractive in the case that the antibonding states get depleted. For transition metals with a high density of d -states just at and *below* the Fermi level the states which are antibonding with respect to the adsorbate surface interaction are pushed above the Fermi level. Thus these antibonding states remain empty level already in the case of a weak H_2 -surface interaction and a small or absent dissociation barrier results.

Feibelman¹⁵ calculated the dependence of the potential energy of a hydrogen molecule in front of a Rh(100) surface in dependence of the orientation of the molecule with respect to the surface metal atoms for fixed heights, Z . He found, that the potential energy variations are governed by the orientation dependence of the bond strength of the H atoms and the metal d -state. The most favorable orientation of the H_2 molecule is not that of the highest symmetry but that optimizing the H–surface bond strength.

Our results confirm the conclusion that the topology of the PES is determined by the direct interaction of the hydrogen molecule with the electronic states of the metal surface. The PES reflects the subtle balance between the weakening of the H–H bond in the molecule and the energy gain connected with the rehybridizing into bonds with the metal substrate^{15,38}. Therefore, it is not unexpected that a correlation exists between the energy at a given height, Z , along the reaction path and the energy and optimal adsorption height of a hydrogen adsorbate at the position of the atoms of the H_2 molecule. The end of the entrance channel regions in Fig. 2 and, hence, the height Z of a hydrogen molecule at which a significant stretching of the intermolecular H–H distance occurs, correlates with the adsorption height of a single hydrogen adatom at the center of mass position (X, Y)²⁹. At large distances, $Z > 1.9$ Å, center-of-mass positions of the hydrogen molecule on-top of a Pd atom are energetically most favorable and center-of-mass position over the hollow site have the lowest gain in potential energy. The direct dissociation with the center-of-mass of the molecule over the bridge site into two neighboring hollow sites ($d_{H-H} = 2.85$ Å) in Fig. 2a is connected with a large, gain in potential energy and a small curvature in the “elbow” plot which is consistent with the large difference in adsorption height and energy between bridge and hollow position²⁹. In the case that the molecule impinges at the hollow site (Fig. 2b) the situation is reversed. The molecule first closely approaches the surface but during the dissociation process the hydrogen atoms move upward to the energetically less favorable bridge positions. Consequently, although the dissociation pathway shown

in Fig. 1b is non-activated as well, the energy gain during dissociation process of the hydrogen molecule is smaller and the curvature in the “elbow” plot is larger. The impact position of the molecule over the on-top site of a surface Pd atom (Fig 2c) is energetically most favorable for larger Z . However, the H–Pd interaction on-top of a metal atom is not strong enough to break the H–H bond without the formation of an energy barrier which is in correspondence with the calculated instability of hydrogen adatoms against associative desorption at on-top sites²⁹.

A more detailed picture of the interaction of a hydrogen molecule with the metal surface may be obtained analyzing the electron density induced by a hydrogen molecule in front of the surface. In Fig. 5 we show the

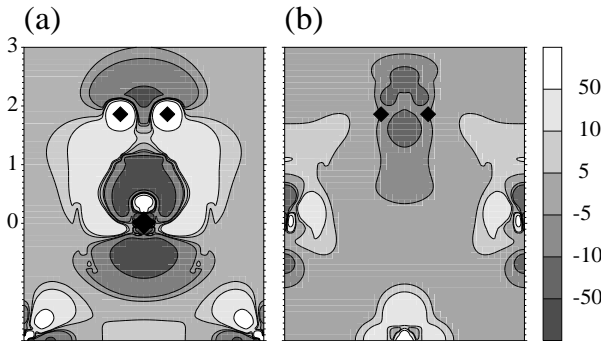


FIG. 5. Difference of the charge density between a hydrogen molecule in front of Pd(100) at a height $Z=1.8$ Å and that of the superposition of the charge density of the clean surface and of free hydrogen molecules. The center-of-mass position of the molecule is over the on-top site (a) and the hollow site (b). The cut plane is perpendicular to the surface and contains the H_2 molecule. The units for the charge density are 10^{-3} Å^{-3} and Å for the height above the surface.

difference of the electron density between a hydrogen molecule in front of Pd(100) at a height $Z=1.8$ Å and that of the superposition of the density of the clean surface and of free hydrogen molecules. Two different configurations are considered. In Fig. 5a the H_2 molecule is over the on-top site and the potential energy has already a large negative value of -0.28 eV and corresponds to the minimum in Fig. 2c. In comparison Fig 5b shows the situation where the H_2 molecule is over the hollow site and the potential energy is close to zero. Figure 5a clearly visualizes that the H_2 –metal surface interaction is connected with a large polarization of both the H_2 molecule and the metal valence electrons. The drop in the potential energy in Fig. 2c is caused by a direct interaction between the σ_g state of the H_2 molecule and the $3z^2 - r^2$ -orbital of the surface Pd atom which has a large density of states just below the Fermi level^{35,36}. There is an occupation redistribution *inside* the d -shell which *depletes* the $3z^2 - r^2$ -orbital thus reducing the Pauli repulsion. Furthermore, holes are introduced into the σ_g state weakening the H–H bond. In addition an increase of electron

density around the center of the H atoms and a more delocalised accumulation of charge density around the Pd atom occurs corresponding to an interaction of the antibonding σ_u^* -orbital of the hydrogen molecule with metal states just above the Fermi level. In the case that the H_2 molecule is shifted from the on-top towards the hollow site in Fig. 5b the interaction with surface Pd d -states having a large density of states just below the Fermi energy is much weaker. The charge density induced around the hydrogen molecule is now more similar to the orthogonalization hole found for hydrogen dissociation at the s, p -metal surface Al(110)⁴⁰. But also in this case there is a considerable depletion of the $3z^2 - r^2$ -orbitals of the surface Pd atoms and an internal occupation conversion inside the d -shell. Due to the weaker polarization of the d -orbitals the potential energy is increased in comparison to the position over the on-top site but also in this case no barrier forms. It is interesting to note, that the polarization pattern in Fig. 5 is close to that deduced from the electronic properties of the *non-interacting* Pd(100) surface using the reactivity function introduced in Ref.³⁶. The induced charge density shown in Fig. 2 is consistent with the reactivity model developed in Ref. 18,34.

V. CONCLUSION

We have calculated the PES of hydrogen dissociation on the clean Pd(100) surface using density functional theory and treating exchange-correlation in the Generalized Gradient Approximation (GGA)²³. The results confirm the presence of several, non-activated dissociation pathways. It is shown that “cartwheel” rotations of the molecular axis out of the favorable orientation parallel to the surface are connected with a large increase of the potential energy, thus confining non-activated dissociation pathways to a small angular region of molecular axis orientations nearly parallel to the surface. “Helicopter” rotations, on the other hand, are hindered mainly because of steric restrictions if the H–Pd distance becomes shorter than a typical H–Pd bonding length. The calculations gave no evidence of a weak molecular bound state, or precursor state, of the H_2 molecule at large distances in front of the surface. There is nearly no repulsion of H_2 molecules in the entrance channel of the reaction pathways even in the case of the activated adsorption pathways and thus no appreciable energy is required for the hydrogen molecule to come close enough to the surface in order to form hydrogen-metal bonds. The observed pronounced differences in the potential energy in dependence of the geometry of the molecule with respect to the surface is governed by the orientation and bond length dependence of the covalent interaction of the hydrogen atoms mainly with the different Pd d -bands. Summarizing these results it is concluded that the dynamics of the hydrogen molecule on the high-dimensional PES cannot be understood using low-dimensional model surfaces

but require a quantum dynamic simulation including all degrees of freedom of the hydrogen molecule. Those calculations have been performed using the calculated PES presented in this paper as an input²².

ACKNOWLEDGMENTS

Discussions with A. Gross are gratefully acknowledged.

* Present Address: Exxon Res. & Eng. Comp., Annandale, NJ, 08801, USA; e-mail: swilke@erenj.com

- ¹ K. D. Rendulic, G. Anger and A. Winkler, Surf. Sci. **208**, 404 (1989).
- ² L. Schröter, G. Ahlers, H. Zacharias and R. David, Phys. Rev. Lett. **62**, 571 (1989).
- ³ L. Schröter, R. David, and H. Zacharias, Surf. Sci. **258**, 259 (1991).
- ⁴ L. Schröter, S. Küchenhoff, R. David, W. Brenig, and H. Zacharias, Surf. Sci. **261**, 243 (1992).
- ⁵ L. Schröter, Chr. Tame, R. David, and H. Zacharias, Surf. Sci. **272**, 229 (1992); L. Schröter, Chr. Tame, J. Gauer, H. Zacharias, R. David and W. Brenig, Faraday Discuss. **96**, 55 (1993).
- ⁶ R. J. Behm, K. Christmann and G. Ertl, Surf. Sci. **99**, 320 (1980).
- ⁷ G. Comsa, R. David and B. J. Schumacher, Surf. Sci. **95**, L210 (1980).
- ⁸ G. R. Darling and S. Holloway, Surf. Sci. **268**, L305 (1992).
- ⁹ *Kinetics of Interface Reactions*, ed. M. Grunze, H. J. Kreuzer, Springer Series in Surface Science **8**, (Springer Verlag, Berlin, Heidelberg, 1987), p. 93.
- ¹⁰ K. D. Rendulic and A. Winkler, Surf. Sci. **299/300**, 261 (1994).
- ¹¹ Ch. Resch, H. F. Berger, K. D. Rendulic and E. Bertel, Surf. Sci. **316** L1105 (1994).
- ¹² P. Alnot, A. Cassuto, and D. A. King, Surf. Sci. **215**, 29 (1990).
- ¹³ St. J. Dixon-Warren, A. T. Pasteur, and D. A. King, Surf. Rev. and Lett. **1**, 593 (1994).
- ¹⁴ A. Gross, J. Chem. Phys. **102**, 5045 (1995).
- ¹⁵ P. J. Feibelman, Phys. Rev. Lett. **67**, 461 (1991).
- ¹⁶ B. Hammer, M. Scheffler, K. W. Jacobsen and J. K. Nørskov, Phys. Rev. Lett. **73**, 1400 (1994).
- ¹⁷ J. A. White, D. M. Bird, M. C. Payne and I. Stich, Phys. Rev. Lett. **73**, 1404 (1994).
- ¹⁸ B. Hammer and M. Scheffler, Phys. Rev. Lett. **74**, 3487 (1995).
- ¹⁹ J. A. White, D. M. Bird and M. C. Payne, submitted to Phys. Rev. B.
- ²⁰ A. Gross, B. Hammer, M. Scheffler, and W. Brenig, Phys. Rev. Lett. **73**, 3121 (1994).
- ²¹ G. R. Darling and S. Holloway, J. Chem. Phys. **101**, 3268 (1994).
- ²² A. Gross, S. Wilke, and M. Scheffler, Phys. Rev. Lett. **75**, 2718 (1995)
- ²³ J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
- ²⁴ P. Blaha, K. Schwarz, and R. Augustyn, WIEN93, Technical University of Vienna 1993.
- ²⁵ Our force calculation follows the description of R. Yu, D. Singh, and H. Krakauer, Phys. Rev. B **43**, 6411 (1991). Further details are given in B. Kohler, S. Wilke, and M. Scheffler, to be published.
- ²⁶ L. Fan and T. Ziegler, J. Am. Chem. Soc. **114** (1992) 10890.
- ²⁷ B. Hammer, K. W. Jacobsen, and J. K. Nørskov, Phys. Rev. Lett. **70** (1993) 3971.
- ²⁸ P. Nachtigall, K. D. Jordan, A. Smith and J. Jónsson, J. Chem. Phys., submitted.
- ²⁹ S. Wilke, D. Hennig, and R. Löber, Phys. Rev. B **50**, 2548 (1994).
- ³⁰ S. Wilke and M. Scheffler, Surf. Sci. **329**, L605 (1995).
- ³¹ M. Petersen, S. Wilke, P. Ruggerone, B. Kohler and M. Scheffler, to be published.
- ³² J. Harris and S. Andersson, Phys. Rev. Lett. **55**, 1583 (1985); J. Harris, Langmuir **7**, 2528 (1991).
- ³³ R. Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*, (VCH Verlag, Weinheim, 1988); Rev. Mod. Phys. **60**, 601 (1988).
- ³⁴ B. Hammer and J. K. Nørskov, preprint
- ³⁵ M. H. Cohen, M. V. Ganduglia-Pirovano and J. Kudrnovský, Phys. Rev. Lett. **72**, 3222 (1994).
- ³⁶ S. Wilke and M. Scheffler, unpublished.
- ³⁷ E. Zaremba and W. Kohn, Phys. Rev. B **15**, 1769 (1976).
- ³⁸ B. I. Lundqvist, O. Gunnarson, H. Hjelmberg, and J. K. Nørskov, Surf. Sci. **89** 196 (1979).
- ³⁹ J.-Y. Saillard and R. Hoffmann, J. Am. Chem. Soc. **106**, 2006 (1984).
- ⁴⁰ B. Hammer, K. W. Jacobsen, and J. K. Nørskov, Phys. Rev. Lett. **70**, 3971 (1993).